

## Synthesis and Characterization of New Ferrocenylamine Sulfide and Selenide Complexes

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(Received June 16, 1988; revised January 5, 1989)

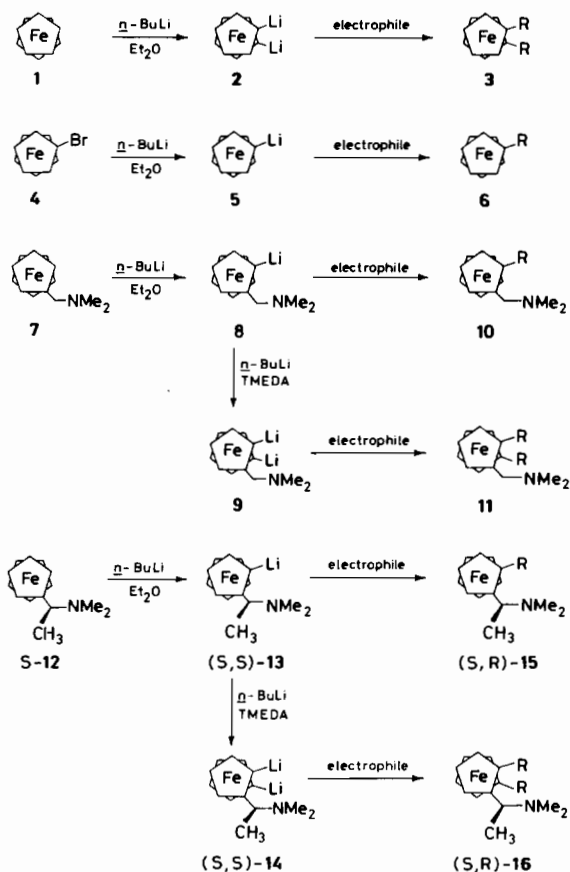
### Abstract

Some hitherto unknown ferrocenylamine sulfides and selenides,  $(\eta^5\text{-C}_5\text{H}_4\text{-SR})\text{Fe}(\eta^5\text{-C}_5\text{H}_3\text{-1-CH}_2\text{NMe}_2\text{-2-SR})$  ( $\text{R} = \text{Et, n-Pr, i-Pr, n-Bu, t-Bu, i-Pent}$ ),  $(R,S)(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3\text{-1-CH(Me)NMe}_2\text{-2-SeR})$  ( $\text{R} = \text{Ph, 4-Cl-Ph}$ ),  $(R,S)(\eta^5\text{-C}_5\text{H}_4\text{-SR})\text{Fe}(\eta^5\text{-C}_5\text{H}_3\text{-1-CH(Me)-NMe}_2\text{-2-SR})$  ( $\text{R} = \text{Et, n-Pr, i-Pr, n-Bu, s-Bu, t-Bu, i-Pent}$ ),  $(R,S)(\eta^5\text{-C}_5\text{H}_4\text{-SeMe})\text{Fe}(\eta^5\text{-C}_5\text{H}_3\text{-1-CH(Me)-NMe}_2\text{-2-SeMe})$ ,  $(S,R)(\eta^5\text{-C}_5\text{H}_4\text{-SR})\text{Fe}(\eta^5\text{-C}_5\text{H}_3\text{-1-CH(Me)NMe}_2\text{-2-SR})$  ( $\text{R} = \text{Et, n-Pr, i-Pr, n-Bu, s-Bu, t-Bu, i-Pent}$ ) and  $(S,R)(\eta^5\text{-C}_5\text{H}_4\text{-SeMe})\text{Fe}(\eta^5\text{-C}_5\text{H}_3\text{-1-CH(Me)NMe}_2\text{-2-SeMe})$  have been synthesized via the lithiation of proper ferrocene precursors, followed by treatment with appropriate disulfides and diselenides. These compounds, which are air stable, have been characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, MS and elemental analysis.

### Introduction (Scheme 1)

A large number of compounds have been synthesized by reaction of lithiation products **2**, **5**, **8**, **9**, **13** and **14** of ferrocene (**1**), bromoferrocene (**4**), [(dimethylamino)methyl]ferrocene (**7**) and [1-(dimethylamino)ethyl]ferrocene (**12**) with different electrophiles. Among the various compound **3** derived from 1,1'-dilithioferrocene (**2**) are those where the electrophilic atom comes from group 14 (**3**,  $\text{R} = \text{organic groups [1] and silyl groups [2]}$ ), group 15 (**3**,  $\text{R} = \text{AsMe}_2, \text{AsPh}_2, \text{PMe}_2, \text{PPh}_2$  [3] and  $\text{P}(\text{t-Bu})_2$  [4]) and transition metals (**3**,  $\text{R} = \text{AuPPh}_3$  [5] and  $\text{Cu}$  [6]). Compounds **6** ( $\text{R} = \text{CO}_2\text{H, SiPh}_3, \text{SiMe}_3, \text{CPh}_2\text{OH}$  [7]) have been synthesized via reaction of proper electrophiles with ferrocenyllithium (**5**) [8]. A wide variety of stereoisomers of **15** and **16** have been prepared [9]. The resolution of **12** into its *R* and *S* enantiomers [10] led to extensive studies of these compounds as chiral ligands in catalysis.

Recently our group reported the synthesis of new ferrocenyl sulfides and selenides [11–16] by using



Scheme 1.

dialkyl, diaryl and dithiuram disulfide and also dimethyl and diaryl diselenide as the electrophiles. These compounds are air stable and have been used as ligands to prepare palladium and platinum complexes, some of which are effective catalysts for asymmetric cross coupling reactions [13, 15]. Also some of the palladium complexes are selective hydrogenation catalysts under homogeneous and heterogeneous conditions for the reduction of diene to monoene [13, 16]. In this work we report the synthesis and characterization of new ferrocenylamine sulfides and selenides. Reaction of various

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disulfides and diselenides as electrophiles with **9**, **13** and **14** yields these previously unknown compounds.

## Experimental

Air-sensitive reagents were manipulated in a prepurified argon or nitrogen atmosphere by using Schlenk techniques. All solvents used were reagent grade and were distilled by standard methods [17]. Proton and carbon-13 NMR spectra were obtained by use of a Bruker WM-250 spectrometer in chloroform- $d_1$  and acetone- $d_6$  respectively. IR spectra were recorded by means of a Perkin-Elmer 599 spectrophotometer. Mass spectra were obtained by use of a Finnigan 4000 instrument with an Incos data system at 70 eV. Melting points were determined by Thomas-Hoover capillary apparatus and are uncorrected.

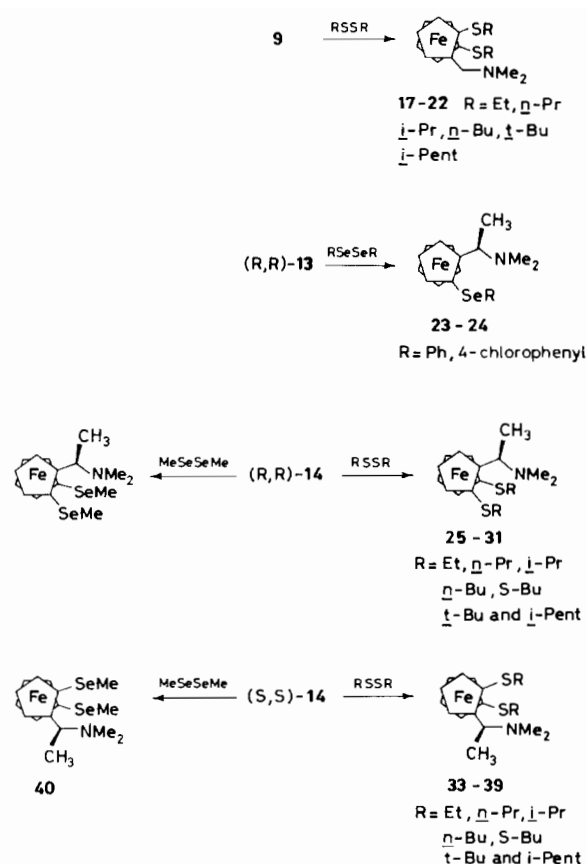
Elemental analyses were performed by Galbraith Laboratories, Inc. Knoxville, TN. Amine **12** was prepared and resolved according to Ugi's procedure [10]. [(Dimethylamino)methyl]ferrocene, dialkyl disulfides, dimethyl and diaryl diselenides, and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were purchased from Aldrich Chemical Company.

### General Procedure for Preparations of Compounds 17–40

All compounds except complexes **23** and **24** were synthesized as follows: A 2.7 M solution of *n*-BuLi in hexane (4.0 ml, 10.8 mmol) was added to a 10 mmol solution of appropriate amineferrocene in 100 ml dry ether at  $-78\text{ }^\circ\text{C}$  under Ar. The orange suspension was warmed to room temperature and stirred for 8 h. Then, a solution of freshly distilled TMEDA (1.20 ml, 10.0 mmol) and *n*-BuLi (4.0 ml, 10.8 mmol) was added to the reaction mixture at  $-78\text{ }^\circ\text{C}$ . After being stirred overnight at room temperature, to the reaction mixture was added dropwise a solution of proper dialkyldisulfide (30 mmol) in 20 ml ether over a 20 min period at  $-78\text{ }^\circ\text{C}$ . The reaction mixture was stirred for 3 h at room temperature, then refluxed for another 12 h. The workup is identical to that reported before [15, 16]. In the case of compounds **23** and **24** diaryl diselenides were added after first lithiation of (*R*)-[1-(dimethylamino)ethyl]ferrocene. Complexes **23** and **24** were both obtained as yellow crystals after recrystallization in acetone. The melting point of compound **23** is  $45\text{ }^\circ\text{C}$  and that of complex **24** is  $92\text{ }^\circ\text{C}$ . All other compounds were obtained as brown oils.

## Results and Discussion (Scheme 2)

Reactions of dialkyl disulfides with 1-[(dimethylamino)methyl]-2,1'-dilithioferrocene (**9**) yield new



Scheme 2.

ferrocenyl sulfides **17–22**. Diaryl diselenides react with 1-[1-(dimethylamino)ethyl]-2-lithioferrocene (**13**) to give ferrocenyl selenides **23** and **24**. 1-[1-(Dimethylamino)ethyl]-2,1'-dilithioferrocene (**14**) react with dialkyl disulfides and dimethyl diselenides, yielding ferrocenyl sulfides (**25–31** and **33–39**) and ferrocenyl selenides (**32** and **40**). It should be noted that compounds **23–40** are chiral with both the central and planar elements of chirality [15, 18]. The yield of reactions are generally high due to the modified procedure adopted [19]. Table 1 presents percentage yields and results of elemental analysis of compounds **17–40**.

### $^1\text{H}$ NMR Spectra

For the 250 MHz  $^1\text{H}$  NMR data for compounds **17–40** see 'Supplementary Material'. The large shift (0.38 ppm) between the two diastereotopic protons of the amino-methylene group of compounds **17–23** in the 3–4 ppm region is an important feature of their  $^1\text{H}$  NMR spectra. For example the value of  $\Delta V/J$  [20] for complex **19** is 6 so there are two clearly defined doublets. The diastereotopic nature of the S-CH<sub>2</sub> protons is another striking feature of these compounds. The two methylene protons with their proper multiplicity present at different chemical

TABLE 1. Yield and microanalytical data for complexes 17–40

Complex	Yield (%)	Analysis: found(calc.) (%)	
		C	H
17	89	56.48(56.19)	6.93(6.93)
18	82	58.48(58.30)	7.53(7.47)
19	81	58.54(58.30)	7.44(7.47)
20	75	59.82(60.13)	7.71(7.93)
21	55	60.59(60.13)	7.97(7.93)
22	78	62.00(61.73)	8.14(8.33)
23	78	58.28(58.28)	5.66(5.62)
24	80	53.81(53.78)	4.95(4.96)
25	92	57.79(57.29)	7.50(7.21)
26	88	59.62(59.25)	7.82(7.71)
27	88	59.52(59.25)	7.83(7.71)
28	88	61.13(60.96)	8.28(8.14)
29	88	61.19(60.96)	8.10(8.14)
30	58	61.09(60.96)	8.15(8.14)
31	75	62.73(62.46)	8.32(8.52)
32	81	43.85(43.37)	5.33(5.23)
33	90	57.38(57.29)	7.37(7.21)
34	83	59.31(59.25)	7.52(7.71)
35	80	59.53(59.25)	7.49(7.71)
36	75	60.35(60.96)	7.93(8.14)
37	73	61.13(60.96)	8.37(8.14)
38	55	61.71(60.96)	8.16(8.14)
39	76	62.18(62.46)	8.13(8.22)
40	82	43.51(43.37)	5.42(5.23)

shifts. The nitrogen methyls appear as a singlet in the 1.99–2.16 ppm range because the inversion of the pyramidal N of NMe<sub>2</sub> is faster than the NMR time scale at room temperature. The upfield peaks of NMe<sub>2</sub> in these compounds are due to the ring current effect. It is difficult to assign substituted Cp ring protons with absolute certainty. <sup>1</sup>H NMR studies [21–23] have proved that any substituent may shield or deshield either positions 2 and 5 or 3 and 4, in any combination relative to ferrocene. Here we have assigned the position of Cp ring protons by comparing with previous results [13–15] and by integration of clearly separated peaks. Assignment of the unsubstituted Cp ring of 23 and 24 is definite. It appears as a singlet at 4.13–4.17 ppm region, due to free rotation about the Fe–Cp axis with very low barrier [24].

### <sup>13</sup>C NMR Spectra

For the carbon-13 NMR data see 'Supplementary Material'. All these compounds have planar chirality and C<sub>1</sub> symmetry [25]. Consequently, groups such as isopropyl methyls are diastereotopic and appear at different positions. Due to fast inversion of two methyl groups in NMe<sub>2</sub>, they are equivalent and appear at the same chemical shift. On the basis of deuterium-labeling studies, Koridze and coworkers [26] have assigned the signals in methoxyl-ferrocene.

Such labeling studies were not performed in this work, so most of the assignments here are tentative. Nevertheless, the assignment of C<sub>1</sub>, C<sub>2</sub> and C'<sub>1</sub> in the Cp rings is reasonable. The chemical shifts of C<sub>2</sub> and C'<sub>1</sub> reflect the inductive and field effects of the substituents (–SR) and (–SeR) and they should be close to each other. Therefore, the most downfield peaks are due to carbon C<sub>1</sub> and two adjacent peaks in the region 77–83 ppm belong to C'<sub>1</sub> and C<sub>2</sub>. The assignment of other carbons of the Cp rings is difficult and based on comparison with previous results [13–16].

### IR Spectra

Compounds 23 and 24 are mono-substituted and obey the 9 and 10 rule [27] which can be expressed as follows. Ferrocene derivatives with an unsubstituted Cp ring, show absorption near 9 μ (1100 cm<sup>-1</sup>) due to an antisymmetric Cp ring breathing mode and near 10 μ (1000 cm<sup>-1</sup>) due to C–H bend parallel to the C<sub>5</sub>H<sub>5</sub> ring, but those with both Cp rings substituted do not exhibit such absorption. Absorption near 890 cm<sup>-1</sup> is indicative of 1,2- (as opposed to 1,3-) disubstituted compounds. Thioethers and selenoethers have generally weak S–C and Se–C stretches around 660 and 510 cm<sup>-1</sup>, respectively.

### Mass Spectra

The mass spectra of compounds 17–40 show molecular ions, expected fragments and smaller peaks consistent with isotopes <sup>32</sup>S, <sup>54</sup>Fe, <sup>57</sup>Fe, <sup>76</sup>Se, <sup>78</sup>Se, <sup>82</sup>Se.

### Supplementary Material

Tables of <sup>1</sup>H and <sup>13</sup>C NMR, infrared absorption frequencies and mass spectra peaks (12 pages) are available from the authors on request.

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